NOVEL ROUTE TO ENANTIOPURE 2,2′-DIARYL-1,1′-BINAPHTHALENES BY STEREOCONSERVATIVE SUZUKI ARYLATION AT POSITIONS 2 AND 2′+

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The Suzuki arylation of enantiopure 2,2′-diiodo-1,1′-binaphthalene affords the 2,2′-diarylated products in considerable yields (up to 52%), however, significantly racemized. The reversed-polarity approach, using novel enantiopure 1,1′-binaphthalene-2,2′-diyldiboronic acid, prepared either by resolution or by stereoconservative boronation, allowed, after optimization of coupling conditions, to obtain the model 2,2′-ditolylated product in good yield (56%) as well, but in addition, without impairing of enantiomeric purity (i.e. stereoconservatively). The developed synthetic approach was found to be an expedient method for the synthesis of enantiopure 2,2′-diaryl-1,1′-binaphthalenes, especially for those with electron-neutral and electron-deficient poor aryl groups. Observing that the diboronic acid decomposes by hydrodeboronation under the reaction conditions, 2-aryl-1,1′-binaphthalenes were isolated as the main products from the reaction with less reactive electron-rich aryl iodides.

Keywords: Biaryls; Binapthyls; Boronic acids; C-C coupling; C_2-Symmetry; Palladium; Steric hindrance; Cross-coupling reactions; Stereoselective synthesis.

Despite the intensive attention paid to the synthesis and application of axially chiral 1,1′-binaphthalene derivatives[2–4], 2,2′-diarylated-1,1′-binaphthalenes **1** have not been readily accessible. Only specific approaches have been successful for the synthesis of particular nonracemic derivatives **1** with aryl, heteroaryl or other cyclic groups attached through C(sp^2) to the positions 2 and 2′ (Scheme 1).

A. stereoselective homocoupling of naphthalenes **2** already substituted at position 2 (to 2,2′-bisoxazolyl-1,1′-binaphthalenes **1A**)[5];

+ Preliminary communication: see ref.[1]

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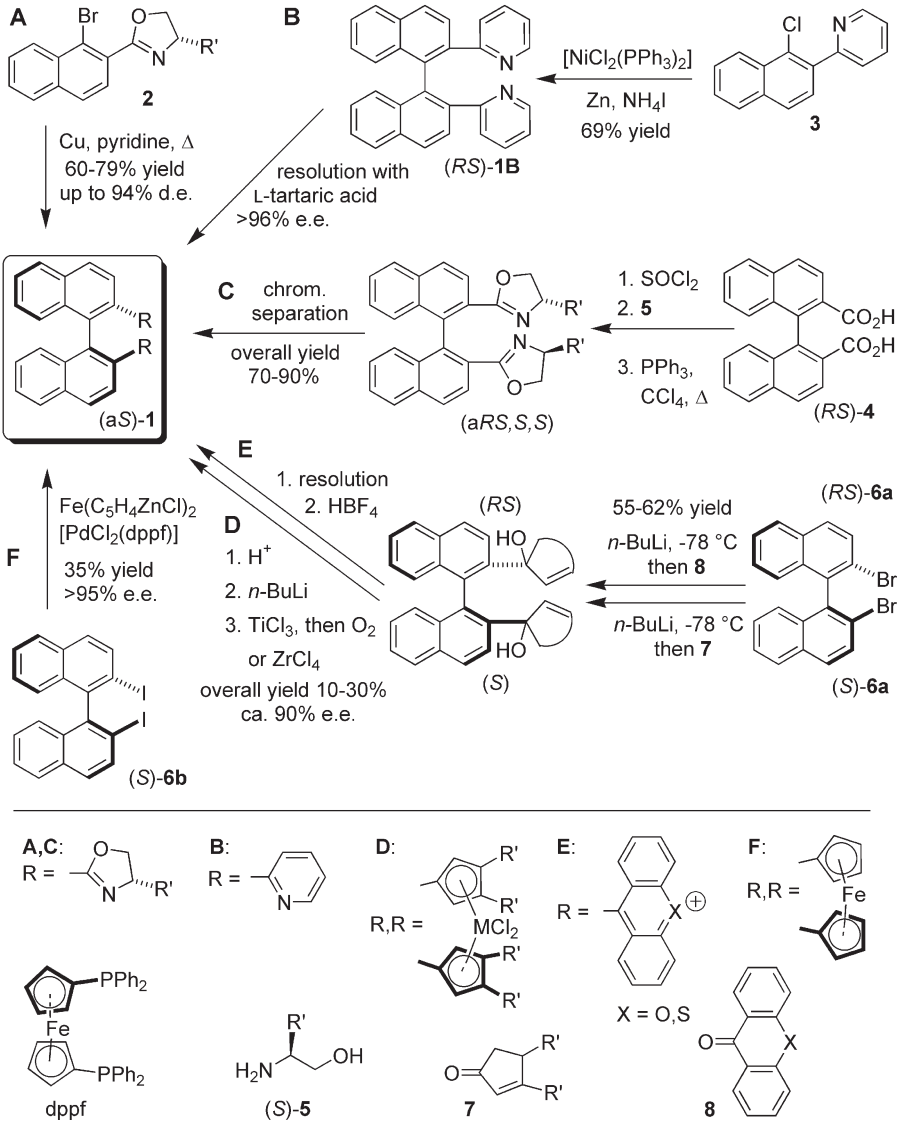
B. nonstereoselective homocoupling of naphthalene **3** already substituted at position 2 followed by resolution (to 2,2′-dipyridyl-1,1′-binaphthalenes **1B**)[6];



SCHEME 1

C. build-up of heterocyclic moieties from carboxy groups of racemic diacid **4** with nonracemic amino alcohol **5**, followed by separation of diasteroisomers (to 2,2′-bisoxazolyl-1,1′-binaphthalenes **1C**)[7];

D. almost stereoconservative substitution at positions 2 and 2′ of enantiomerically pure dibromide **6a** via lithiation, quenching of lithium intermediate with cyclic enones **7**, followed by aromatization and metallation (to *ansa*-metallocenes **1D**)[8] (This approach is specific because it uses an electrophile not readily reacting with butyllithium, so the electrophile can be added before lithiation is completed and the substitution takes place stepwise – as the first at position 2, then at position 2′ – avoiding significant racemization via configurationally unstable dilithium intermediate.);

E. approach similar to *D*, from racemic dibromide **6a** via lithiation and reaction with xanthenone **8** or its thio analogue, followed by resolution and aromatization (to 2,2′-bis(xanthylium/thioxanthylium)-1,1′-binaphthalenes **1E**)[9];

F. stereoconservative Negishi cross-coupling at positions 2 and 2′ of enantiopure diiodide **6b** (to *ansa*-ferrocene **1F**)[10].

The approach *F*, direct cross-coupling arylations at positions 2 and 2′, would be the best candidate for the simple and effective synthesis. However, in many variations (Kumada, Negishi, Suzuki or Stille), it did not afforded di-2-pyridyl derivative **1B**[6]. Also attempts of Suzuki arylations of diboronic acid **9** or dibromide **6a** gave no or only traces of desired diarylated products, respectively[11], and monoarylated derivatives **10** were isolated as the main products in these cases. All the attempts mentioned here were reported to be performed only from racemic binaphthalene substrates.

However, reported cross-coupling reactions (Suzuki, Stille, Negishi) on 1,1′-binaphthalene derivatives at any other positions than 2 and 2′ (most often at positions 3 and 3′[12] or 6 and 6′[13] on derivatives substituted at positions 2 and 2′ to ensure configurational stability), as a rule proceed smoothly, affording corresponding diarylated products in good to high yields without impairing enantiopurity (stereoconservatively).

The peculiarity of the cross-coupling reactions (or any substitutions) at positions 2 and 2′ consist in substantial steric hindrance (due to bulky 2-substituted 1-naphthyl group at position adjacent to the reaction site) and the risk of racemization during the reaction, since these reactions take place at positions where a nonbonding interaction between groups (being replaced in the course of the reaction) is decisive for configurational stability of these derivatives.

With the aim to prepare the diarylated binaphthalenes **1** with potential application either in stereoselective synthesis (as new chiral ligands), supra-

molecular chemistry (as chiral building blocks), or in materials science (chiral compounds with specific optical or electronic properties), the method used for their synthesis should be tolerant of functional groups in order to allow direct introduction of already functionalized aryl groups. This requirement together with the known low sensitivity to steric hindrance[14] (required as mentioned above) is fulfilled by the Suzuki reaction[15]. This reaction is of special interest, since organoboronic acids, used as an organometallic component in this reaction, are easily available, non-toxic and inert to air and water. Therefore we focused our effort on the elaboration of an access to enantiopure derivatives **1** using this cross-coupling reaction.

RESULTS AND DISCUSSION

2,2′-Dihalo-1,1′-binaphtalenes Approach (6)

2,2′-Dihalo-1,1′-binaphthalenes (dibromide **6a**, diiodide **6b**) and bistriflate **6c** (as their synthetic equivalent), available in enantiopure form, are suitable as potential substrates for cross-coupling reactions. First, we tried the Suzuki arylation of more easily accessible bistriflate **6c** with phenylboronic acid, but it did not gave detectable amounts (TLC) of desired diarylated product **1G** under any conditions (various Ni and Pd catalysts, solvents and bases). Traces of monoarylated product and binaphthol monotriflate as a product of partial hydrolysis of bistriflate **6c**, if barium hydroxide was used as a base, were identified as the only new compounds in the reaction mixture.

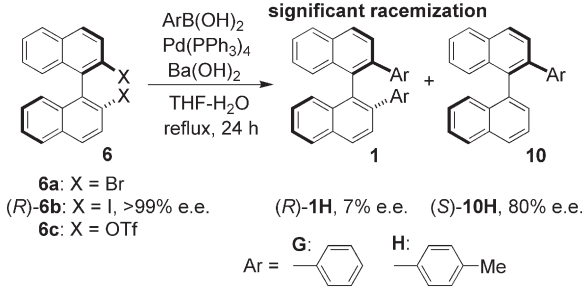
Using barium hydroxide as base, we succeeded in obtaining the desired diarylated products **1G** and **1H** either from dibromide **6a** or diiodide **6b** in considerable yields (up to 52%, in contrast to only traces reported so far[11]), together with small amounts of monoarylated products **10G** and **10H** (Table I).

However, starting from enantiopure diiodide **6b**, the obtained product **1H** was found to be almost racemic (Table I, 7% e.e.). Racemization during this reaction is most probably caused by specific mechanistic pathway including configurationally unstable Pd(IV) intermediate which has been reported elsewhere[10].

On the other hand, only minor racemization was observed in the formation of monoarylated product **10H** (80% e.e.). The formation of monotolylated product **10H** is prevailingly stereoconservative (conserving spatial

arrangement of the binaphthalene moiety) although the stereochemical descriptor has changed[2,16] (applying CIP system rules).

TABLE I
Suzuki arylation of binaphthalene precursors **6**[a]



Entry	Substrate	Ar	Isolated, %	
			1	**10**
1	**6c**	**G**, phenyl	–	–
2	**6a**	**G**, phenyl	38	11
3	**6b**	**G**, phenyl	44	19
4	**6a**	**H**, 4-methylphenyl	46	32
5	(*R*)-**6b**[b]	**H**, 4-methylphenyl	52[c]	10[d]

[a] 0.5 mmol **6**, 1.2 mmol $ArB(OH)_2$, 0.05 mmol $[Pd(PPh_3)_4]$, 3 mmol $Ba(OH)_2 \cdot 8H_2O$, 4 ml THF–H_2O (1:1), reflux, 24 h; acid work-up followed by flash chromatography. [b] >99% e.e. (HPLC). [c] 7% e.e. (HPLC). [d] 80% e.e. (HPLC).

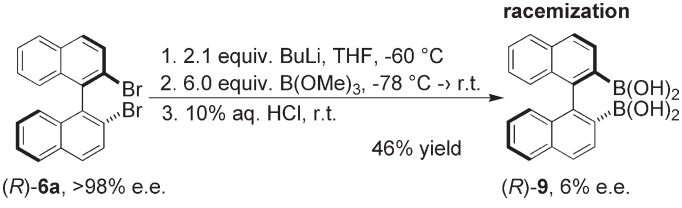
1,1′-Binaphthalene-2,2′-diyldiboronic Acid Approach

Being encouraged by acceptable yields in the Suzuki arylation of diiodide **6b** mentioned above (significantly higher than those reported so far), we decided to investigate an approach with reversed polarity of the substrates for cross-coupling, starting from diboronic acid **9** and aryl halides. In addition, the assumed mechanism for this approach should be a standard one, without any intermediate causing atropisomerization of the binaphthalene moiety, with the reactions taking place independently at both the positions. However, the preparation of the required enantiomerically pure diboronic acid **9** has not been described. On the other hand, a greater variety

of aryl halides that can be used as reagents in this approach, are available than those of arylboronic acids applicable in the former polarity approach.

*Preparation of Enantiopure Diboronic Acid **9***

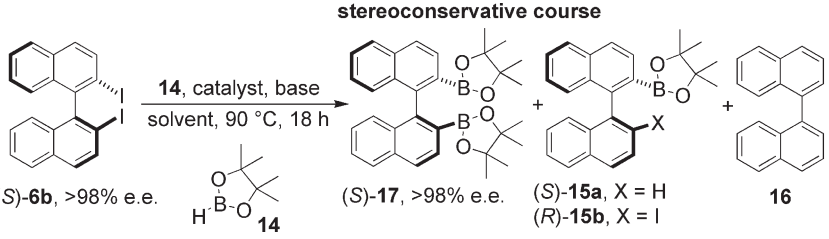
Racemic diboronic acid **9** was prepared by Kaufmann et al.[17] by lithiation of racemic dibromide **6a** and quenching of the generated dilithio derivative with a large excess of trimethyl borate. The approach using quenching of 2,2′-dilithio-1,1′-binaphthalene, prepared from enantiopure dibromide **6a** below –40 °C (which is an aproximate limit for configurational stability of the dilithium compound[18]), with electrophiles was successfull in preparation of nonracemic silicon[19], mercury[20] and tin[21] 2,2′-dimetallo-1,1′-binaphthalenes. However, quenching with most of electrophiles, for instance with chlorodiphenylphosphine even at –95 °C [22], gives almost racemic binaphthalene derivatives. Using this approach, starting from enantiopure dibromide **6a** and performing the lithiation and quenching with trimethyl borate at low temperatures, allowed us to isolate almost racemic diboronic acid **9** (Scheme 2).



SCHEME 2

Therefore we examined another approach – the most frequently used alternative route to arylboronic acids, which consist in palladium-catalyzed boronation of aryl halides in the presence of amine as a base[23]. Starting from a more reactive dihalobinaphthalene – diiodide **6b**, we used pinacol boronate (**14**) as a boronation agent, most often applied palladium catalysts and amines, and various solvents (Table II). Monoboronates **15a** and **15b** together with completely hydrodehalogenated product – binaphthalene **16**, were prevailing products in the reaction mixture in all cases. Full conversion of diiodide **6b** was observed only in toluene (entries 4–6). Desired diboronate **17** was isolated in low yield using the combination of catalyst, amine and solvent given in entry 6. Nevertheless, when taking enantiopure diiodide (*S*)-**6b**, the isolated diboronate **17** was found to be enantiopure (determined with diboronic acid **9**, obtained from diboronate **17** by alkaline hydrolysis).

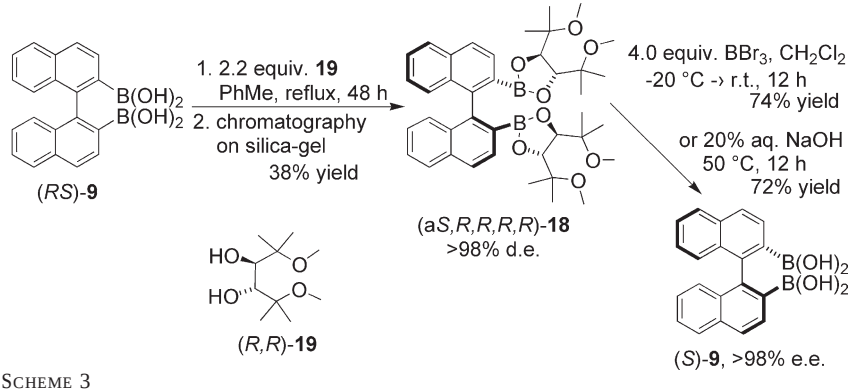
TABLE II
Atempts of boronation of **6b** with dioxaborolane **14**[a]



Entry	Catalyst	Base	Solvent	Isolated, %			
				17	**15a**	**15b**	**16**
1	$[PdCl_2(dppf)]$	Et_3N	$ClCH_2CH_2Cl$	–	10	5	10
2	$[PdCl_2(dppf)]$	*i*-Pr_2NH	1,4-dioxane	–	12	2	12
3	$[PdCl_2(dppf)]$	*i*-$PrEt_2N$	THF	–	5	–	38
4	$[PdCl_2(PPh_3)_2]$	Et_3N	toluene	<3	35	5	35
5	$[PdCl_2(dppf)]$	*i*-Pr_2NEt	toluene	<3	21	30	15
6	$[PdCl_2(dppf)]$	Et_3N	toluene	17	67	2	5

[a] 0.5 mmol (*S*)-**6b**, 2–3 mmol **14**, 0.05 mmol catalyst, 3 mmol base, 3 ml solvent, stirring at 90 °C for 18 h; mild acid work-up followed by flash chromatography.

We succeeded in more effective preparation of enantiopure diboronic acid **9** by resolution of racemic **9**, performed by chromatographic separation of the diastereoisomers of its ester **18** with chiral diol **19** accessible from L-tartaric acid (Scheme 3). The diastereoisomeric purity of diboronate



SCHEME 3

18 was easily determined from its ^{1}H NMR spectra and, after flash chromatography twice on silica gel, it was found to be >98% d.e. (Fig. 1). Both acid and alkaline hydrolysis afforded enantiopure diboronic acid **9**. The yield and purity of the isolated product were higher in the case of acid hydrolysis, since prolonged heating of diboronic acid **9** leads to partial decomposition by hydrodeboronation.

Enantiomeric purity of diboronic acid **9**, obtained from each experiment mentioned above, was determined at first by comparison of its optical rotation with that of enantiopure **9**, obtained by resolution, and then by enantioselective HPLC of product **1H** of the subsequent Suzuki arylation. The absolute configurations of compounds **9** and **18** were assigned on the basis of the sign of optical rotation of product **1H** prepared from **9**, compared with that of the partly enriched product **1H** obtained from diiodide **6b** of known configuration.

Isolation and characterization of diboronic acid **9** is quite troublesome, as was already mentioned by Kaufmann et al.[17] Its precipitation from aqueous acid medium is not complete, and a very fine precipitate is formed. Precipitations with hexanes from concentrated dichloromethane solution yield a mixture of diboronic acid **9** with its anhydrides. Chromatographic purification of **9** on silica gel causes partial hydrodeboronation. However, esters of **9**, i.e. **17** and **18** do not decompose during chromatography. Therefore it is most advantageous to purify **9** in the form of an ester, to isolate crude diboronic acid **9** after hydrolysis by precipitation from dichloromethane and to directly use the crude product in the Suzuki reaction.

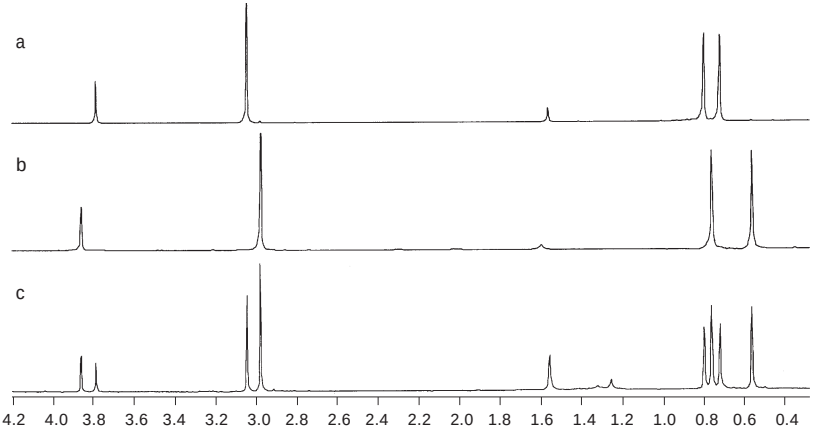


FIG. 1
Expansions of ^{1}H NMR spectra of (a*R*,*R*,*R*,*R*)-**18** (a), (a*S*,*R*,*R*,*R*,*R*)-**18** (b) and their mixture (c)

Cross-Couplings

Optimization of Coupling Conditions

Over thousand papers dealing with the Suzuki cross-coupling reaction have been already published, where a wide variety of combinations of catalysts, bases and solvents were used[15,24]. For optimization of coupling conditions in the reaction of diboronic acid **9** with model tolyl iodide, we examined the most frequently used palladium catalysts (Table III), bases (Table IV)

TABLE III
Optimization of catalyst for the Suzuki arylation of diboronic acid **9**[a]

Entry	Catalyst	Isolated, %
1	$[Pd(dba)_2]$	<3
2	$[Pd(OAc)_2]$	<3
3	$[Pd(dppe)_2]$	10
4	$[Pd(dppp)_2]$	10
5	$[Pd(dppf)_2]$	25
6	$[Pd(PPh_3)_4]$	56

[a] 0.5 mmol **9**, 1.2 mmol 4-$CH_3C_6H_4I$, 0.05 mmol catalyst, 3 mmol $Ba(OH)_2 \cdot 8H_2O$, 5 ml THF–H_2O (5:1), reflux, 24 h; acid work-up followed by flash chromatography.

TABLE IV
Optimization of base for the Suzuki arylation of diboronic acid **9**[a]

Entry	Base	Isolated, %
1	KF	7
2	CsF	<3
3	Na_2CO_3	0
4	Cs_2CO_3	28
5	K_3PO_4[b]	<3
6	Bu_4NOH[c]	39
7	$Ba(OH)_2$	52

[a] 0.5 mmol **9**, 1.2 mmol 4-$CH_3C_6H_4I$, 0.05 mmol $[Pd(PPh_3)_4]$, 3 mmol base, 5 ml THF, reflux, 24 h; acid work-up followed by flash chromatography. [b] Toluene used as solvent, the reaction temperature 70 °C. [c] 3 mmol Bu_4NOH in 1 ml of methanol was used as base.

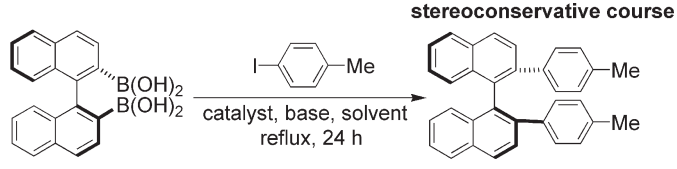
and solvents (Table V). Although monoarylated product **10H** and binaphthalene **16** were observed in the resulting reaction mixtures, only the target diarylated product **1H** were monitored. The results obtained clearly showed the combination of $[Pd(PPh_3)_4]$, barium hydroxide and aqueous tetrahydrofuran being the best, allowing to obtain the desired product **1H** in considerable 56% yield (compared with failure of this approach reported so far[11]).

TABLE V
Optimization of solvent for the Suzuki arylation of diboronic acid **9**[a]

Entry	Solvent	Isolated, %
1	MeOH	44
2	PhMe	54
3	dioxane	25
4	THF	52
5	THF–MeOH (5:1)	52
6	THF–H_2O (5:1)	56

[a] 0.5 mmol **9**, 1.2 mmol 4-$CH_3C_6H_4I$, 0.05 mmol $[Pd(PPh_3)_4]$, 3 mmol $Ba(OH)_2 \cdot 8H_2O$, 5 ml solvent, stirring at 70 °C for 24 h; acid work-up followed by flash chromatography.

In addition, when using these optimized conditions in the reaction starting from enantiopure diboronic acid **9** (prepared by resolution, >98% e.e.), the isolated product **1H** was found to be enantiopure as well (HPLC on Chiralcel Daicel OD-H column, >99% e.e.) (Scheme 4).



(*S*)-**9**, >98% e.e. (*S*)-**1H**, >99% e.e.

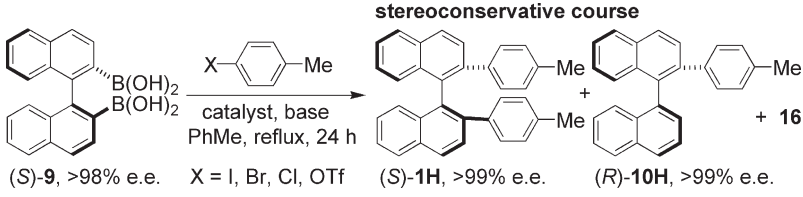
SCHEME 4

The Suzuki coupling of tolyl iodide with the stereoisomerically pure diboronates (*S*)-**17** and (a*S*,*R*,*R*,*R*,*R*)-**18**, performed under the same conditions as with diboronic acid **9**, afforded enantiopure desired diarylated product (*S*)-**1H** in 42 and 12% yields, respectively. Therefore, it is advantageous to perform the couplings with free diboronic acid **9**, giving the desired product (*S*)-**1H** in higher yield (56%).

Scope and Limitations – Variation of Aryl Substrates

After optimization of coupling conditions and verifying of stereoconservative course of this reaction, we intended to determine the scope and limitations of the discovered method for the preparation of enantiopure 2,2′-diaryl-1,1′-binaphthalenes (**1**). First, we examined the effect of leaving group of tolyl substrates (Table VI). The found dependence of the yield of the desired diarylated product **1H** in palladium-catalyzed reactions (entries 1–4) corresponds to the known general reactivity of aryl halides and triflates in the palladium-catalyzed Suzuki reaction decreasing in the order: I > Br > OTf > Cl, resulting from the relative reactivity of respective aryl substrates in oxidative addition to a palladium(0) complex[25]. Since slow decomposition of diboronic acid 9, which takes place under the reaction conditions (heating in strongly alkaline medium), is a competitive reaction, relative reactivity of aryl substrates affects the yield of the diarylated product **1H**. In accordance, increasing amounts of hydrodeboronated products (monoarylated **10H** and binaphthalene **16**) were observed in the reaction mixture with decreasing yield of the diarylated product **1H**. The use of a

TABLE VI
Suzuki arylation of diboronic acid **9** with various tolyl electrophiles[a]



Entry	X	Catalyst	Base	Isolated, %	
				1H[b]	**10H**
1	I	$[Pd(PPh_3)_4]$	$Ba(OH)_2$	54	<3
2	Br	$[Pd(PPh_3)_4]$	$Ba(OH)_2$	40	10
3	Cl	$[Pd(PPh_3)_4]$	$Ba(OH)_2$	3	27
4	OTf	$[Pd(PPh_3)_4]$	$Ba(OH)_2$	21	41
5	Cl	$[Ni(PPh_3)_4]$	$Ba(OH)_2$	–	23
6	OTf	$[Ni(PPh_3)_4]$	CsF	–	38

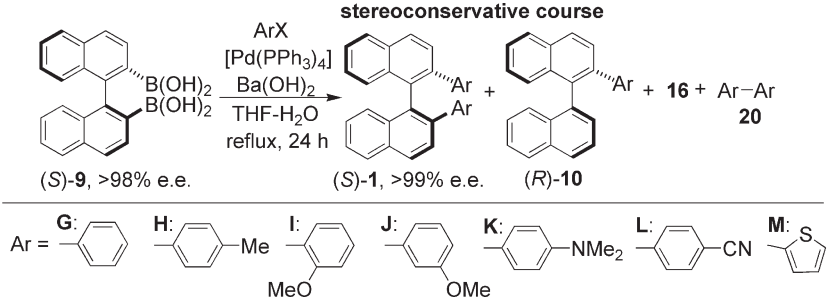
[a] 0.5 mmol **9**, 1.2 mmol 4-$CH_3C_6H_4X$, 3 mmol base, 0.05 mmol $[Pd(PPh_3)_4]$, 5 ml PhMe, reflux, 24 h; acid work-up followed by flash chromatography. [b] >99% e.e. (HPLC).

nickel catalyst in the case of less reactive aryl substrates in palladium-catalyzed arylations – tolyl chloride and triflate (entries 5, 6) – did not lead to the formation of detectable amounts of the diarylated product **1H**.

The stereoconservative course of the tolylation reaction was proved by enantioselective HPLC for both ditolylated and monotolylated products **1H** and **10H**. Despite the spatial arrangement of the binaphthalene moiety does not change during the formation of both the products, the stereodescriptor denoting its absolute configuration has changed in the case of **10H**.

Thereafter, we examined exploitability of this reaction for the preparation of various enantiopure 2,2′-diaryl-1,1′-binaphthalenes (**1**) by variation of aryl groups in aryl halides (Table VII). Based on the results given above, we preferably used aryl iodides.

TABLE VII
Suzuki arylation of diboronic acid **9** with various aryl halides[a]



Entry	Ar	X	Isolated, %	
			1	**10**
1	phenyl (**G**)	I	46[b]	<5
2	4-methylphenyl (**H**)	I	56[b]	<5
3	2-methoxyphenyl (**I**)	I	–	35
4	3-methoxyphenyl (**J**)	I	12[b]	37
5	(dimethylamino)phenyl (**K**)	Br	15[b]	24
6	4-cyanophenyl (**L**)	I	35[b]	<5
7	2-thienyl (**M**)	I	43[b]	<5

[a] 0.5 mmol (*S*)-**9**, 1.2 mmol ArX, 0.05 mmol $[Pd(PPh_3)_4]$, 3 mmol $Ba(OH)_2 \cdot 8H_2O$, 6 ml THF–H_2O (5:1), reflux, 24 h; acid work-up followed by flash chromatography. [b] >99% e.e. (HPLC).

The desired diarylated products **1** were obtained in considerable yields from the reactions of **9** with aryl iodides possessing sufficient reactivity in oxidative addition to a palladium(0) complex: in the highest yields (from 35 to 56%) in the case of electron-neutral and electron-deficient aryls (phenyl **G**, tolyl **H**, cyanophenyl **L** and thienyl **M**; entries 1, 2, 6 and 7), and in lower yields (12–15%) with aryls bearing electron-donating groups (3-methoxy **J** and 4-(dimethylamino) **K**, entries 4 and 5). Formation of diarylated product **1** was not observed in the reaction of more sterically demanding *ortho*-substituted aryl iodide (2-methoxyphenyl **I**; entry 4). In all cases, the reaction mixtures were quite complex, containing monoarylated derivatives **10** (being the main products in the case of electron-rich aryls **I**–**K**, entries 3–5), binaphthalene **16**, homocoupling products – biaryls **20** and low amounts of other not identified products inseparable by flash chromatography in sufficiently pure form. The yields of arylated products **1** were not remarkably improved when the corresponding aryl halides were used in a higher excess (4 mmol, i.e. four-fold excess relative to one boronic group). All arylated products **1** and **10** obtained in sufficient amount were fully characterized. Particular signals (of methoxy group and neighbouring hydrogen or carbon atoms) in NMR spectra of monoarylated 2-methoxyphenyl derivative **10I** were broad due to atropisomerization (rotation around the binaphthalene-aryl bond) and therefore the spectra are given at 50 °C, at which all signals were sharp.

The subsequent enantioselective HPLC of all diarylated products **1** (**1G**, **1H**, **1J**, **1K**, **1L** and **1M**), prepared from enantiopure diboronic acid **9**, proved the stereoconservative course of the reaction, finding them to be enantiopure (>99%).

CONCLUSION

We have developed an expedient method for the synthesis of a new group of enantiopure 1,1′-binaphthalene derivatives – 2,2′-diarylated derivatives **1**. Only few of them have been prepared by special methods so far. Proper choice of the reaction conditions and the polarity of the substrates were found to be crucial for obtaining these derivatives in enantiopure forms and considerable yields (up to 56%). This approach is expedient especially for the synthesis of diaryl derivatives **1** with electron-neutral or electron-deficient aryl groups. It is limited to the synthesis of diaryl derivatives **1** that do not bear *ortho*-substituent on aryl group being introduced. Applications of the prepared functionalized diarylated derivatives **1** after transformation to suitable chiral ligands, supramolecular synthons or functional

materials, are the subject of intensive study in our laboratory. Other applications of the novel enantiomerically pure diboronic acid **9** are also under investigation.

EXPERIMENTAL

Flash column chromatography was performed on Merck Silica Gel (60H). Merck Silica Gel F254 plates were used for thin layer chromatography and visualization was effected with UV light (254 nm). Melting points were measured on a Kofler block; they are uncorrected. Specific optical rotations were measured on a Perkin–Elmer 241 polarimeter and are given in deg cm^3 g^{-1} dm^{-1}. HPLC analysis was made on a Chiralcel Daicel OD-H column using a Jasco CD-995 detector (CD and UV detection) or UV-VIS detector LCD 5000. UV-VIS spectra (in nm) were measured on a Hewlett–Packard diode array 8245 spectrophotometer. CD spectrum (in nm) was measured on a Jasco J710 instrument. IR data were recorded on a Specord M 80 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 300 instrument at 298 K. Chemical shifts (δ) are reported in ppm downfield to internal standard TMS (δ 0.00 ppm) and the solvent was used as a reference. Working frequency was 300 MHz for ^{1}H and 75.5 MHz for ^{13}C NMR. Coupling constants (*J*) are given in Hz. GC-MS spectra (70 eV, 150 μA, EI) were recorded on a Voyager GC/MS Finnigan instrument. Elemental analyses were determined with an Erba Science 1106 instrument.

All chemicals were used as purchased if not stated otherwise. Dichloromethane was dried with calcium chloride under argon. THF, toluene, dioxane and diethyl ether were dried with sodium/benzophenone. All solvents for coupling reactions were degassed with a thaw-freeze pump in 3 cycles and these reactions were performed under nitrogen using the Schlenk technique. Dibromide (*RS*)- and (*R*)-**6a** [26], diiodide (*RS*)-, (*R*)- and (*S*)-**6b** [26], bistriflate (*RS*)-**6c** [27], diboronic acid (*RS*)-**9** [17] and diol (*R,R*)-**19** [28] were prepared according to the literature procedures.

(*R*)-2,2′-Dibromo-1,1′-binaphthalene (**6a**)

M.p. 155–157 °C (hexanes–toluene), $[\alpha]_D^{23}$ 33.2 (*c* 1.24, pyridine), >98% e.e. (polarimetry) (lit.[26] m.p. 157–157.5 °C, $[\alpha]_D^{21.4}$ +33.1 (*c* 1.00, pyridine)).

(*R*)- and (*S*)-2,2′-Diiodo-1,1′-binaphthalene (**6b**)

(*R*)-**6b**: m.p. 227–229 °C (hexanes), $[\alpha]_D^{23}$ +16.7 (*c* 1.75, pyridine), >99% e.e. (determined by HPLC) (lit.[26] m.p. 225–227 °C, $[\alpha]_D^{23}$ +16.4 (*c* 1.725, pyridine)). (*S*)-**6b**: $[\alpha]_D^{22}$ –16.2 (*c* 1.75, pyridine), >99% e.e. (determined by HPLC). (*RS*)-**6b**: HPLC: Chiralcel Daicel OD-H column, eluent *n*-heptane with 1% 1,2-dimethoxyethane (DME), temperature 16 °C, flow rate 1.0 ml/min, pressure 31 bar, detector (UV) λ = 280 nm; *k′*: 6.52 (*S*)-**6b**, 7.35 (*R*)-**6b**.

Nonracemic 1,1′-Binaphthalene-2,2′-diyldiboronic Acid (**9**)

A dry two-necked flask was charged with 0.480 g of (*R*)-**6a** (1.17 mmol, >96% e.e.). The flask was evacuated, filled with argon and capped with septum. 20 ml of absolute THF was added and cooled to –78 °C. 1.25 ml of 2 M BuLi in hexanes (2.5 mmol, 2.14 equiv.) was added dropwise to the stirred reaction mixture. After addition, the mixture was stirred for 1 h at

–60 °C. Another dry flask was charged with 1.2 g $B(OMe)_3$ (1.35 ml, 11.8 mmol, 10 equiv.) and 30 ml absolute THF and the stirred solution was cooled to –78 °C. The solution of dilithiated dibromide was added dropwise via cannula to the latter solution at –78 °C during 1 h. The reaction mixture was stirred at –78 °C for another hour and then was allowed to warm up to room temperature and stirred at this temperature for 10 h. The solvent was evaporated and 50 ml of diethyl ether, 50 ml of aqueous 1 M HCl were added to the yellow residue, the mixture was vigorously stirred to hydrolyze for one hour and then the layers were separated. The water layer was extracted three times with 30 ml portions of diethyl ether. Combined organic layers were washed with saturated aqueous $NaHCO_3$ (30 ml) and water (30 ml) and dried over anhydrous Na_2SO_4. After filtration and evaporation, the yellowish residue was dissolved in 2–3 ml CH_2Cl_2, precipitated with ca. 20 ml of hexanes and centrifuged several times. Product **9** was obtained as a white solid 184 mg (46%) (melting point determination is not possible because of the formation of oligomeric anhydrides). ^1H and ^{13}C NMR spectra were in agreement with literature values[17]. Enriched (*R*)-**9**: $[\alpha]_D^{23}$ +5.4 (*c* 0.34, $CHCl_3$), 6% e.e.

(*S*)-2,2′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-binaphthalene (**17**)

A dry Schlenk flask, capped with a rubber septum, was flame-dried under vacuum, backfilled with argon and cooled to room temperature. The flask was charged with (*S*)-**6b** (253 mg, 0.5 mmol, >98% e.e.) and $[PdCl_2(dppf)]$ (36.7 mg, 0.05 mmol) and the flask was evacuated again and backfilled with argon. 2 ml toluene, 420 µl Et_3N (305 mg, 3 mmol, 6 equiv.) were successively injected into the flask, followed by **14** (78 mg, 346 µl, 2 mmol, 2 equiv.). The reaction mixture switched from orange to brownish and was heated to 90 °C and stirred overnight. After cooling, the reaction mixture was poured into 10% aqueous NH_4Cl and extracted three times with CH_2Cl_2 (10 ml portions). Combined organic fractions were washed twice with water and brine and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was chromatographed on silica gel (eluent hexanes–ethyl acetate, gradient 10:0–9:1) (Table II).

(*S*)-17: colorless oil, $[\alpha]_D^{22}$ –35.5 (*c* 0.83, $CHCl_3$) (product **1H** of subsequent Suzuki reaction: >99% e.e. as determined by HPLC). Spectral data were in agreement with literature values[17]. (*RS*)-**17**: m.p. 63–65 °C (lit.[17] m.p. 65 °C).

(S)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-binaphthalene (**15a**). White crystalline solid, m.p. 110–112 °C, $[\alpha]_D^{22}$ –50.4 (*c* 1, $CHCl_3$). Spectral data were in agreement with literature values[17]. (*RS*)-**15a**: m.p. 54–56 °C (lit.[16] m.p. 53–54 °C).

(R)-2-Iodo-2′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-binaphthalene (**15b**). Isolated only as a mixture with **15a**. ^1H NMR (300 MHz, $CDCl_3$): 7.94–7.82 m, 4 H; 7.98–7.75 m, 2 H; 7.15–7.50 m, 5 H; 7.05 d, 1 H, ^3J = 8.4; 0.93 s, 6 H (CH_3); 0.83 s, 6 H (CH_3).

(a*S,R,R,R,R*)- and (a*R,R,R,R,R*)-2,2′-Bis[4,5-bis(1-methoxy-1-methylethyl)-1,3,2-dioxaborolan-2-yl]-1,1′-binaphthalene (**18**)

A dry flask was charged with (*RS*)-**9** (300 mg, 0.88 mmol), (*R,R*)-**19** (400 mg, 1.95 mmol) and a grain of TsOH. The flask was evacuated and back-filled with nitrogen. Deoxygenated toluene 40 ml was injected and a Dean–Stark apparatus was attached. The reaction mixture was refluxed for 24 h under nitrogen with removal of water. Then the solvent was evaporated under vacuum. A crude residue was purified by flash chromatography. Combined esters were obtained from the third fraction (198 mg) of the first chromatography on silica gel (eluent

hexanes–ethyl acetate, gradient from 100:0 to 80:20), the ratio of esters was 10:8. The next two flash chromatographies on silica gel (eluent hexanes–ether 6:1) first gave (a*S*,*R*,*R*,*R*)-**18** (86 mg, 38%) as a colorless oil, $[\alpha]_D^{27}$ +25.7 (*c* 0.27, $CHCl_3$), >98% d.e. (determined by ^{1}H NMR), R_F 0.38 (hexanes–diethyl ether, 4:1). UV-VIS (MeOH): 228, 286, 296, 321. IR ($CHCl_3$): 3055, 1715, 1608, 1550, 1520, 1480, 1432, 1422, 1402, 1380, 1352, 1245, 1210, 1113, 1105, 1012, 950, 846, 712, 680, 648. ^{1}H NMR (300 MHz, $CDCl_3$): 7.93 d, 2 H, ^3J = 8.3 (Ar-H); 7.87 d, 2 H, ^3J = 8.2 (Ar-H); 7.85 d, 2 H, ^3J = 8.3 (Ar-H); 7.41 ddd, 2 H, *J* = 2.2, 6.6, 8.3 (Ar-H); 7.15 m, 4 H (Ar-H); 3.78 s, 4 H (C-H); 3.04 s, 12 H (OCH_3); 0.80 s, 12 H (CH_3); 0.72 s, 12 H (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 146.69, 134.50, 133.74, 130.60, 127.68, 127.38, 126.33, 126.23, 125.33, 82.40, 75.59, 49.53, 20.88, 18.77. For $C_{40}H_{52}B_2O_8$ (682.4) calculated: 70.40% C, 7.68% H; found: 70.69% C, 7.74% H. As a second was eluted (a*R*,*R*,*R*,*R*)-**18** (72 mg, 25%), colorless oil, $[\alpha]_D^{27}$ –41.1 (*c* 0.44, $CHCl_3$), >98% d.e. (determined by ^{1}H NMR), R_F 0.36 (hexanes–diethyl ether, 4:1). UV-VIS (MeOH): 228, 286, 296, 320. CD (MeOH): 332 (–m), 313 (+m), 302 (+s), 278 (–s), 272 (+m), 266 (–w), 262 (+m), 254 (–m), 249 (+w). IR ($CHCl_3$): 3050, 1725, 1605, 1550, 1520, 1485, 1432, 1417, 1402, 1380, 1340, 1250, 1210, 1113, 1100, 1012, 950, 846, 712, 680, 650. ^{1}H NMR (300 MHz, $CDCl_3$): 8.05 d, 2 H, ^3J = 8.3 (Ar-H); 7.90 d, 2 H, ^3J = 8.3 (Ar-H); 7.86 d, 2 H, ^3J = 8.2 (Ar-H); 7.40 ddd, 2 H, *J* = 2.2, 5.6, 8.3 (Ar-H); 7.13 m, 4 H (Ar-H); 3.86 s, 4 H (CH); 2.98 s, 12 H (OCH_3); 0.76 s, 12 H (CH_3); 0.56 s, 12 H (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 147.14, 134.85, 133.58, 131.12, 127.55, 127.42, 126.37, 126.22, 125.47, 82.20, 75.51, 49.47, 20.95, 18.37. GC-MS (EI), *m/z* (%): [M^+] not observable, 341 (26), 340 (92), 267 (73), 265 (100), 252 (60). $C_{40}H_{52}B_2O_8$ (682.4) calculated: 70.40% C, 7.68% H; found: 70.25% C, 7.62% H.

Acid Hydrolysis of **18**

A solution of BBr_3 (906 mg, 350 µl, 3.6 mmol) in 2 ml of absolute CH_2Cl_2 was added dropwise to a cool solution (–20 °C) of either (a*S*,*R*,*R*,*R*)- or (a*R*,*R*,*R*,*R*)-**18** (76 mg, 0.11 mmol, >98% d.e.) in 3 ml of absolute CH_2Cl_2. While stirring under nitrogen, the reaction mixture was warmed up to room temperature overnight. Then it was carefully poured onto ice and extracted three times with CH_2Cl_2 (10 ml portions). Combined organic layers were washed with 2% aqueous HCl, water and dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated to ca. 1 ml and this solution was precipitated with hexanes several times. The white precipitate was dried under vacuum, yielding 28 mg (74%) of pure (*S*)- or (*R*)-**3**. (*R*)-**3**: $[\alpha]_D^{25}$ +86.3 (*c* 0.27, $CHCl_3$). (*S*)-**3**: $[\alpha]_D^{25}$ –87.3 (*c* 0.31, $CHCl_3$).

Alkaline Hydrolysis of **18**

A mixture of either (a*S*,*R*,*R*,*R*)- or (a*R*,*R*,*R*,*R*)-**18** (89 mg, 0.13 mmol, >98% e.e.) and 5 ml of aqueous 20% NaOH was stirred at 50 °C overnight. After cooling, the reaction mixture was acidified with 6 M HCl and extracted three times with CH_2Cl_2 (10 ml portions). Combined organic layers were washed with water and dried over anhydrous Na_2SO_4. The filtrate was concentrated to ca. 1 ml and precipitated with hexanes several times to yield white precipitate 31.5 mg (72%), impure (*S*)- or (*R*)-**9.**

General Procedure for the Suzuki Coupling of **6**

A Schlenk flask, capped with a rubber septum, was charged with **6a** or **6b** (0.5 mmol), phenyl- or (4-methylphenyl)boronic acid (1.2 mmol), $Ba(OH)_2 \cdot 8H_2O$ (946.4 mg, 3 mmol)

and [$Pd(PPh_3)_4$] (57.8 mg, 0.05 mmol), the flask was evacuated and backfilled with argon. 2 ml of water and 2 ml of THF were succesively injected into the flask and the mixture was heated to 60 °C overnight while stirring. After cooling, the reaction mixture was poured into 5% aqueous HCl and extracted three times with CH_2Cl_2 (10 ml portions). Combined organic fractions were washed twice with water and brine and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was chromatographed on silica gel (Table I).

General Procedure for the Suzuki Coupling of **9**

A Schlenk flask was charged with (*R*)- or (*S*)-**9** (170.5 mg, 0.5 mmol), aryl iodide (1.2 mmol), $Ba(OH)_2 \cdot 8H_2O$ (946.4 mg, 3 mmol) and [$Pd(PPh_3)_4$] (57.8 mg, 0.05 mmol). The flask was evacuated and backfilled with argon. 1 ml water and 5 ml THF were succesively injected into the flask and the mixture was heated to reflux overnight while stirring. After cooling, the reaction mixture was poured onto aqueous 5% HCl and extracted three times with CH_2Cl_2 (10 ml portions). Combined organic fractions were washed twice with water and brine and dried over anhydrous Na_2SO_4. After filtration and evaporation the solvent, the residue was chromatographed on silica gel (Table VII).

(S)-2,2′-Diphenyl-1,1′-binaphthalene (**1G**). White solid, m.p. 125–128 °C, $[\alpha]_D^{22}$ –128.5 (*c* 1, $CHCl_3$), >99% e.e. (determined by HPLC), R_F 0.42 (hexanes–ethyl acetate, 10:1). UV (hexanes): 226, 248, 290. IR ($CHCl_3$): 1620 m, 1520 m, 1470 w, 1280 w, 1050 m, 880 w, 840 s, 720 s, 680 w. ^{1}H NMR (300 MHz, $CDCl_3$): 7.92 d, 2 H, ^3J = 8.0; 7.88 d, 2 H, ^3J = 8.4; 7.50–7.28 m, 8 H; 7.00 dd, 2 H, ^3J = 7.3, 7.3; 6.86 dd, 4 H, ^3J = 7.7, 8.4; 6.43 d, 4 H, ^3J = 7.7. ^{13}C NMR (75 MHz, $CDCl_3$): 141.4, 139.6, 134.6, 134.3, 132.3, 129.1, 128.5, 128.1, 128.0, 127.5, 127.0, 126.5, 126.1, 125.5. GC-MS (EI), *m/z* (%): 406 (100) [M^+], 329 (36), 326 (31), 315 (23). For $C_{32}H_{22}$ (406.4) calculated: 94.08% C, 5.92% H; found: 93.02% C, 6.61% H. (*RS*)-**1G**: m.p. 228–230 °C. HPLC: Chiralcel Daicel OD-H column, eluent *n*-heptane with 1% DME, temperature 21 °C, flow rate 1.0 ml/min, pressure 47 bar, detector (UV) λ = 280 nm; *k′*: 0.84 (*S*)-**1G**, 1.19 (*R*)-**1G**.

(S)-2,2′-Bis(4-methylphenyl)-1,1′-binaphthalene (**1H**). White solid, m.p. 179–183 °C, $[\alpha]_D^{22}$ –169.8 (*c* 1.01, $CHCl_3$), >99% e.e. (determined by HPLC), R_F 0.45 (hexanes–ethyl acetate, 10:1). UV (hexanes): 226, 256, 294. IR ($CHCl_3$): 3045, 1620, 1600, 1520, 1510, 1220, 1120, 1030, 870, 820, 720. ^{1}H NMR (300 MHz, $CDCl_3$): 7.91 d, 2 H, ^3J = 8.1; 7.97 d, 2 H, ^3J = 8.4; 7.23–7.48 m, 8 H; 6.69 d, 4 H, ^3J = 7.8; 6.36 d, 4 H, ^3J = 8.1; 2.18 s, 6 H (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 140.0, 139.0, 136.0, 135.0, 134.6, 132.6, 129.4, 129.0, 128.4, 128.2, 128.1, 127.9, 126.8, 125.7, 31.3. GC-MS (EI), *m/z* (%): 434 (100) [M^+], 326 (26), 343 (24), 163 (18). For $C_{34}H_{26}$ (434.58) calculated: 93.94% C, 6.06% H; found: 94.04% C, 5.57% H. (*RS*)-**1H**: m.p. 184–186 °C. HPLC: Chiralcel Daicel OD-H column, eluent *n*-heptane with 1.5% DME, temperature 21 °C, flow rate 1.0 ml/min, pressure 50 bar, detector (UV) λ = 280 nm; *k′*: 4.03 (*S*)-**1H**, 4.96 (*R*)-**1H**.

(R)-2,2′-Bis(3-methoxyphenyl)-1,1′-binaphthalene (**1J**). White solid, m.p. 126–130 °C, $[\alpha]_D^{21}$ +143.3 (*c* 1, $CHCl_3$), >99% e.e. (determined by HPLC), R_F 0.32 (petroleum ether–ethyl acetate, 10:1). IR ($CHCl_3$): 3015 m, 1590 s, 1480 m, 1460 s, 1420 m, 1280 m, 920 m, 820 s, 690 m. UV (MeOH (log ε)): 226 (5.86); 252 (5.60); 296 (5.28). ^{1}H NMR (300 MHz, $CDCl_3$): 7.96 d, 2 H, ^3J = 8.1; 7.92 d, 2 H, ^3J = 8.4; 7.36–7.52 m, 8 H; 6.85 dd, 2 H, ^3J = 7.9, 9.1; 6.66 d, 2 H, *J* = 8.1; 6.10 d, 2 H, ^3J = 7.6; 6.00 s, 2 H; 3.15 s, 6 H (OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 158.3, 142.6, 139.6, 134.6, 134.3, 132.3, 128.4, 128.1, 128.0, 127.5, 126.6, 125.6,

124.8, 121.6, 113.5, 113.1, 54.1. GC-MS (EI), *m/z* (%): 466 (100) [$M^{\bullet+}$], 313 (26), 326 (16). (*RS*)-**1J**: m.p. 135–138 °C. HPLC: Chiralcel Daicel OD-H column, eluent *n*-heptane with 20% DME, temperature 21 °C, flow rate 1.0 ml/min, pressure 47 bar, detector (UV) λ = 280 nm; *k'*: 2.09 (*S*)-**1J**, 2.67 (*R*)-**1J**.

(R)-2,2'-Bis[4-(dimethylamino)phenyl]-1,1'-binaphthalene (**1K**). White solid, m.p. 195–198 °C, $[\alpha]_D^{20}$ +12.1 (*c* 0.01, $CHCl_3$), >99% e.e. (determined by HPLC), R_F 0.29 (hexanes–ethyl acetate, 4:1). UV-VIS (*c* 1.30 × 10^{-5} M, MeOH (log ε)): 222 (4.41), 290 (3.97). IR ($CHCl_3$): 1610, 1520, 1420, 1410, 1350, 1220, 925, 700. ^{1}H NMR (300 MHz, $CDCl_3$): 7.90 d, 2 H, ^3J = 8.2; 7.9 d, 2 H, ^3J = 8.5; 7.48–7.35 m, 6 H, ^3J = 8.5; 7.28 m, 2 H, ^3J = 6.7; 6.42 d, 4 H, ^3J = 8.8; 6.29 d, 4 H, ^3J = 8.8; 2.81 s, 12 H (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 149.1, 139.0, 134.8, 134.3, 132.2, 130.4, 130.0, 129.1, 128.1, 127.8, 127.6, 126.4, 125.2, 111.8, 40.8. For $C_{36}H_{32}N_2$ (492.7) calculated: 87.77% C, 6.55% H, 5.69% N; found: 87.22% C, 6.57% H, 5.55% N. (*RS*)-**1K**: m.p. 270–280 °C with decomposition. HPLC: Chiralcel Daicel OD-H column, eluent *n*-hexane with 10% propan-2-ol, temperature 16 °C, flow rate 0.5 ml/min, pressure 18 bar, detector (UV) λ = 254 nm; *k'*: 3.97 (*S*)-**1K**, 4.91 (*R*)-**1K**.

(R)-2,2'-Bis(4-cyanophenyl)-1,1'-binaphthalene (**1L**). White solid, m.p. 86–90 °C, $[\alpha]_D^{20}$ +105.8 (*c* 0.01, $CHCl_3$), >99% e.e. (determined by HPLC), R_F 0.15 (hexanes–ethyl acetate, 4:1). UV-VIS (*c* 9.98 × 10^{-5} M, MeOH (log ε)): 222 (4.83), 272 (4.70). IR ($CHCl_3$): 2220, 1600, 1490, 1440, 1200, 1030, 920, 840, 820, 690. ^{1}H NMR (300 MHz, $CDCl_3$): 8.00 d, 2 H, ^3J = 8.2; 7.98 d, 2 H, ^3J = 8.2; 7.58 d, 2 H, ^3J = 8.2; 7.40 2 × d, 2 × 2 H; 7.33 d, 2 H, ^3J = 8.2; 7.19 dd, 4 H, ^3J = 8.2; 6.50 d, 4 H, ^3J = 8.2. ^{13}C NMR (75 MHz, $CDCl_3$): 146.0, 137.8, 134.4, 134.1, 132.9, 131.3, 129.8, 129.4, 128.7, 127.7, 127.6, 127.4, 126.8, 119.0, 110.4. GC-MS (EI), *m/z* (%): 456 (100) [M^+], 351 (22), 338 (10). (*RS*)-**1L**: 300–310 °C with decomposition. HPLC: Chiralcel Daicel OD-H column, eluent *n*-hexane with 10% propan-2-ol, temperature 16 °C, flow rate 0.75 ml/min, pressure 27 bar, detector (UV) λ = 254 nm; *k'*: 5.23 (*S*)-**1L**, 6.78 (*R*)-**1L**.

(S)-2,2'-Di-2-thienyl-1,1'-binaphthalene (**1M**). White off solid, m.p. 155–159 °C, $[\alpha]_D^{21}$ +15.7 (*c* 1, $CHCl_3$), >99% e.e. (determined by HPLC), R_F 0.32 (hexanes–ethyl acetate, 10:1). UV-VIS (*c* 9.98 × 10^{-5} M, MeOH (log ε)): 222 (4.83), 272 (4.70), 302 (4.39). Spectral data were in agreement with literature values[29]. For $C_{28}H_{20}S_2$ (418.6) calculated: 80.35% C, 4.33% H, 15.32% S; found: 79.47% C, 4.04% H, 14.56% S. (*RS*)-**1O**: m.p: 195–200 °C (acetone–water) (lit.[29] m.p. 204–206 °C). HPLC: Chiralcel Daicel OD-H column, eluent *n*-heptane with 1% DME, temperature 21°C, flow rate 1.0 ml/min, pressure 47 bar, detector (UV) λ = 280 nm; *k'*: 5.84 (*S*)-**1M**, 6.35 (*R*)-**1M**.

2-Phenyl-1,1'-binaphthalene (**10G**). White solid, m.p. 131–133 °C (lit.[11] m.p. 133 °C), R_F 0.52 (hexanes–chloroform, 4:1). Spectral data were in agreement with literature values[11].

(R)-2-(4-Methylphenyl)-1,1'-binaphthalene (**10H**). White solid, m.p. 110–111 °C, $[\alpha]_D^{22.5}$ –133 (*c* 1, $CHCl_3$), >99% e.e. (determined by HPLC), R_F 0.52 (hexanes–chloroform, 4:1). Spectral data were in agreement with literature values[11]. (*RS*)-**10H**: m.p. 121–123 °C (lit.[11] m.p. 123 °C). HPLC: Chiralcel Daicel OD-H column, eluent *n*-hexane with 1% DME, temperature 17 °C, flow rate 1.0 ml/min, pressure 32 bar, detector (UV) λ = 254 nm; *k'*: 3.03 (*R*)-**10H**, 4.29 (*S*)-**10H**.

2-(2-Methoxyphenyl)-1,1'-binaphthalene (**10I**). White solid, m.p. 54–58 °C, R_F 0.38 (hexanes–chloroform, 4:1). UV-VIS (*c* 5.08 × 10^{-5} M, MeOH (log ε)): 222 (4.97), 285 (3.14). IR ($CHCl_3$): 1590, 1580, 1490, 1460, 1430, 1370, 1200, 1120, 1020, 920, 700. ^{1}H NMR (50 °C, 300 MHz, $CDCl_3$): 7.99 d, 1 H, ^3J = 8.2; 7.95 d, 1 H, ^3J = 8.2; 7.80 d, 1 H, ^3J = 8.2; 7.73 d, 1 H, ^3J = 8.2; 7.57 d, 1 H, ^3J = 8.2; 7.55–7.15 m, 9 H, ^3J = 8.2; 7.0 dd, 1 H, ^3J = 8.2, 7.7; 6.60 br, 2 H;

3.8–3.0 br s, 3 H (OCH_3). ^{13}C NMR (50 °C, 75 MHz, $CDCl_3$): 156.5, 137.2, 136.9, 136.8, 133.4, 133.3, 132.9, 130.9, 129.1, 128.3, 128.1, 128.1, 128.0, 127.5, 127.5, 127.4, 127.3, 126.8, 126.2, 126.0, 125.7, 125.6, 125.5, 125.1, 119.8, 110.3, 54.9. GC-MS (EI), *m/z* (%): 360 (100) [M^+], 345 (10), 326 (19), 313 (17), 252 (15), 156, (21).

2-(3-Methoxyphenyl)-1,1′-binaphthalene (**10J**). White solid, m.p. 89–94 °C, R_F 0.42 (hexanes–chloroform, 4:1). UV-VIS (*c* 2.54 × 10^{-5} M, MeOH (log ε)): 224 (4.50), 292 (4.42). IR ($CHCl_3$): 1580, 1580, 1460, 1420, 1370, 1280, 1200, 1020, 900, 690. ^1H NMR (300 MHz, $CDCl_3$): 8.05 d, 1 H, ^3J = 8.6; 7.94 d, 1 H, ^3J = 8.2; 7.85 d, 1 H, ^3J = 8.6; 7.80 d, 1 H, ^3J = 8.2; 7.68 d, 1 H, ^3J = 8.6; 7.35–7.48 m, 4 H; 7.18–7.30 m, 4 H; 6.75 ddd, 1 H, *J* = 8.6, 1.7, 1.0; 6.60–6.52 m, 2 H; 3.2 s, 3 H (OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 158.7, 143.4, 139.5, 137.3, 135.9, 134.0, 133.5, 133.4, 132.8, 129.1, 128.7, 128.4, 128.2, 128.1, 128.0, 127.7, 127.4, 126.8, 126.5, 126.3, 125.9, 125.8, 125.7, 121.9, 114.2, 113.3, 54.8. GC-MS (EI), *m/z* (%): 360 (100) [M^+], 326 (15), 313 (27), 300 (10), 289 (11), 252 (18), 156 (24).

2-[4-(Dimethylamino)phenyl]-1,1′-binaphthalene (**10K**). Yellowish solid, m.p. 95–99 °C, R_F 0.45 (hexanes–ethyl acetate, 4:1). UV-VIS (*c* 1.38 × 10^{-5} M, MeOH (log ε)): 224 (5.13), 284 (3.65). IR ($CHCl_3$): 1680, 1610, 1530, 1500, 1350, 1210, 1130, 1010, 940, 900, 810, 690, 660. ^1H NMR (300 MHz, $CDCl_3$): 7.97 d, 1 H, ^3J = 8.8; 7.91 d, 1 H, ^3J = 8.2; 7.87 d, 1 H, ^3J = 8.2; 7.81 d, 1 H, ^3J = 8.2; 7.67 d, 1 H, ^3J = 8.2; 7.45–7.36 m, 4 H; 7.30–7.14 m, 4 H; 6.95 d, 2 H, ^3J = 8.8; 6.38 d, 2 H, ^3J = 8.7; 2.78 s, 6 H ($N(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): 137.4, 135.2, 133.6, 133.4, 133.3, 132.3, 131.7, 130.1, 129.1, 129.0, 128.6, 128.2, 128.1, 128.0, 127.9, 127.8, 127.4, 127.0, 126.7, 126.1, 126.0, 125.5, 125.4, 112.8, 41.2. GC-MS (EI), *m/z* (%): 373 (100) [M^+], 327 (12), 313 (9), 163 (14).

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